UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2011/2012

Januari 2012

EBS 336/3 – Analytical Chemistry
[Kimia Analitis]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains SEVENTEEN printed pages and TWO pages APPENDIX before you begin the examination.
[Sila pastikan bahawa kertas peperiksaan ini mengandungi TUJUH BELAS muka surat yang bercetak dan DUA muka surat LAMPIRAN sebelum anda memulakan peperiksaan ini.]

This paper consists of SEVEN questions.
[Kertas soalan ini mengandungi TUJUH soalan.]

Instruction: Answer **FIVE** questions. If candidate answers more than five questions only the first five questions answered in the answer script would be examined.
*[**Arahan**: Jawab **LIMA** soalan. Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.]*

The answers to all questions must start on a new page.
[Mulakan jawapan anda untuk semua soalan pada muka surat yang baru.]

You may answer a question either in Bahasa Malaysia or in English.
[Anda dibenarkan menjawab soalan sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.]

In the event of any discrepancies, the English version shall be used.
[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.]

…2/-

1. [a] A hydrogen peroxide solution (H_2O_2) is analyzed by adding a slight excess of standard $KMnO_4$ solution and back titrating the unreacted $KMnO_4$ with standard Fe^{2+} solution. About 0.587 g sample of the H_2O_2 solution is taken, 25.0 mL of 0.0215 M $KMnO_4$ is added and the back titration requires 5.10 mL of 0.112 M Fe^{2+} solution.
Given: At. wt.: Fe = 55.85; H = 1.0; O = 16.0 and Mn = 54.9 g/mol

Given the reaction equation:

$5H_2O + 2MnO_4^{2-} + 6H^+ \longrightarrow 50_2 + 2Mn^{2+} + 8H_2O$

$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Satu larutan hidrogen peroksida (H_2O_2) dianalisiskan dengan menambahkan sedikit lebihan larutan piawai $KMnO_4$ dan melakukan pentitratan-balik $KMnO_4$ yang tidak bertindakbalas itu dengan larutan piawai Fe^{2+}. Sebanyak 0.587 g sampel dari larutan H_2O_2 itu diambil dan 25.0 mL 0.0215 M larutan $KMnO_4$ ditambahkan dan pentitratan-balik memerlukan sebanyak 5.10 mL 0.112 M larutan Fe^{2+}.
Diberikan: JAR : Fe = 55.85; H = 1.0; O = 16.0 dan Mn = 54.9 g/mol

Diberikan persamaan tindakbalas berikut:

$5H_2O + 2MnO_4^{2-} + 6H^+ \longrightarrow 50_2 + 2Mn^{2+} + 8H_2O$

$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

What is the percent of H_2O_2 in the sample?

Berapakah peratus H_2O_2 dalam sampel?

(30 marks/*markah*)

[b] Coke is an impure form of carbon that is often used in the industrial production of metals from their oxides. If a sample of coke is 95% carbon by mass, determine the mass of coke needed to react completely with 1.0 ton of copper (II) oxide.

Kok adalah karbon yang tak tulen yang biasa digunakan dalam industri penghasilan logam dari oksidanya. Jika satu sampel kok mengandungi karbon dengan jisim 95%, tentukan jisim kok yang diperlukan untuk bertindakbalas sepenuhnya dengan 1.0 ton kuprum (II) oksida.

Given the reaction equation:
Diberikan persamaan tindakbalas:

$$2CuO_{(s)} + C_{(s)} \rightarrow 2Cu_{(s)} + CO_{2(g)}$$

Given: At wt. Cu = 64 g/mol; O = 16g/mol; C = 12 g/mol
Diberikan: JAR bagi Cu = 64 g/mol; O = 16g/mol; C = 12 g/mol

(40 marks/*markah)*

[c] In the nuclear industry, detailed records are kept of the plutonium received, transported or used. Each shipment of plutonium pellets received is carefully analyzed to check that the purity and hence the total quantity is as the supplier claims. A particular shipment is analyzed with the following results: 99.93, 99.87, 99.91 and 99.86%.
The listed purity as received from the supplier is 99.95%.
Is the shipment acceptable?

Dalam industri nuklear, rekod terperinci bagi plutonium yang diterima, dipindahkan atau digunakan disimpan. Setiap bekalan pelet plutonium dianalisa dengan teliti untuk mengesahkan bahawa ketulenan dan seterusnya kuantiti totalnya adalah seperti yang dinyatakan oleh pembekal. Suatu bekalan dianalisa dan keputusan adalah seperti berikut: 99.93, 99.87, 99.91 dan 99.86%.
Ketulenan yang diterima daripada pembekal adalah 99.95%.
Adakah bekalan ini boleh diterima?

(30 marks/*markah*)

2. [a] A limestone sample weighing 400 mg was dissolved in acid and treated with excess sodium oxalate. The solution was made basic and the resulting calcium oxalate precipitate was filtered, washed and redissolved in dilute acid. The solution required 14.1 mL of 0.00865 M $KMnO_4$ for titration. What is the calcium content of the limestone?

Satu sampel batu kapur dengan berat 400 mg dilarutkan dalam asid dan dirawat dengan natrium oksalat berlebihan. Larutan itu kemudiannnya dijadikan bes dan mendakan kalsium oksalat yang terbentuk dituras, dicuci dan dilarutkan semula dalam asid cair. Larutan ini memerlukan 14.1 mL isipadu larutan 0.00865 M $KMnO_4$ bagi pentitratan. Apakah kandungan kalsium dalam batu kapur ini?

Given the reaction equation:
Diberikan persamaan tindakbalas:

$$5\ H_2C_2O_4 + 2\ MnO_4^- + 6H^+ \rightarrow 10\ CO_2 + 8\ H_2O + 2\ Mn^{2+}$$

(40 marks/*markah)*

[b] In the Liebig titration of cyanide ion, a soluble complex is formed; and at the equivalence point, solid silver cyanide is formed, signaling the end point.

Reaction Equation:

$2\ CN^- + Ag^+ \rightarrow Ag(CN)_2^-$ (Titration)

$Ag(CN)_2^- + Ag^+ \rightarrow Ag[Ag(CN)_2]$ (End point)

About 0.4723 g sample of KCN was titrated with 0.1025 M $AgNO_3$, requiring 34.95 mL. What is the percent purity of the KCN?

Dalam pentitratan Liebig ion sianida, satu kompleks yang terlarutkan terbentuk pada takat ekuivalen, pepejal argentum sianida terbentuk, menandakan takat akhir.

Persamaan Tindakbalas:

$2\ CN^- + Ag^+ \rightarrow Ag(CN)_2^-$ *(Pentitratan)*

$Ag(CN)_2^- + Ag^+ \rightarrow Ag[Ag(CN)_2]$ *(Takat akhir)*

Pentitratan satu sampel KCN dengan berat 0.4723 g memerlukan sebanyak 34.95 mL 0.1025 M $AgNO_3$. Apakah peratus ketulenan KCN ini?

Given: At. wt. K = 39.10; C = 12; N = 14, Ag = 107.87 g/mol.

Diberikan: JAR bagi K = 39.10; C = 12; N = 14, Ag = 107.87 g/mol.

(30 marks/*markah)*

[c] A ship of copper ore from Chile was purchased by a local metal refiner. The analysis certificate, made out while the ship was being loaded, showed that % Cu is 14.66 with a standard deviation of 0.07% for 5 measurements. When the ore arrived at the refinery, it was analyzed with the following results: % Cu = 14.58, 14.61, 14.69, and 14.64. Should the refiner accept the ore? Refer to APPENDIX.

Satu kapal yang membawa bijih kuprum telah dibeli oleh satu syarikat penulenan logam tempatan. Sijil analisis yang dikeluarkan, menunjukkan % Cu adalah 14.66 dengan sisihan piawai sebanyak 0.07 % bagi 5 pengukuran. Apabila bijih ini sampai di tempat penulenan, ianya dianalisiskan dengan bacaan berikut: % Cu = 14.58, 14.61, 14.69 dan 14.64. Perlukah syarikat penulenan ini menerima bijih ini? Rujuk pada LAMPIRAN.

(30 marks/*markah*)

3. [a] In an experiment to determine the iron content of a sample of steel, 1.40 g of the metal were dissolved by boiling in acid. The iron in the solution was then all converted into the +2 oxidation state and the solution was made up to 100.0 cm^3 using dilute sulphuric acid. 10.0 cm^3 aliquot of this solution were titrated against a 0.02 mol/dm^{-3} solution of potassium permanganate. About 24.2 cm^3 of the potassium permanganate solution were required to reach the end-point of the titration.

The reaction occurring in the titration is:

$5Fe^{2+}$ (aq) + MnO_4^- (aq) + 8 H^+ (aq) → $5Fe^{3+}$ (aq) + Mn^{2+} (aq) + $4H_2O$ (l)

Dalam satu eksperimen untuk menentukan kandungan ferum dalam satu sampel keluli, 1.40 g logam dilarutkan dengan cara pendidihan dalam asid. Kemudian semua ferum dalam larutan ditukarkan kepada keadaan pengoksidaan +2 dan larutan dicairkan kepada isipadu 100.0 cm^3 menggunakan asid sulfurik cair. 10.0 cm^3 alikuot larutan ini dititratkan dengan larutan 0.02 mol/dm^{-3} kalium permanganat. Sebanyak 24.2 cm^3 larutan kalium permanganat diperlukan untuk mencapai takat akhir pentitratan.

Tindakbalas yang berlaku dalam pentitratan adalah:

$5Fe^{2+}$ (ak) + MnO_4^- (ak) + 8 H^+ (ak) → $5Fe^{3+}$ (ak) + Mn^{2+} (ak) + $4H_2O$ (c)

(i) Calculate the mass of iron in the sample of steel (At. Wt. Fe: 56.0)
Kirakan jisim ferum dalam sampel keluli (JAR Fe: 56.0)

(25 marks/*markah*)

(ii) Calculate the percentage by mass of iron in the steel.
Kirakan peratus jisim ferum dalam keluli.

(25 marks/*markah*)

[b] (i) 25.0 mL aliquot of river water was treated with a mild reducing agent followed by excess 2,9-dimethyl-1,10-phenanthroline. This reagent reacts with copper but not iron (II). After diluting to 50.0 mL, the solution had an absorbance of 0.388 at 455 nm. From the calibration curve, this absorbance corresponded to a concentration of 3.1 ppm Cu. Calculate the copper concentration in parts per million in the original sample.
Given: At. wt.: Cu = 63.54 g/mol

25.0 mL alikuot air sungai telah dirawat dengan satu agen penurunan dan kemudiannya 2,9-dimetil-1,10-penantrolin ditambah berlebihan. Reagen ini hanya bertindakbalas dengan kuprum tetapi bukan dengan ferum (II). Selepas pencairan kepada 50.0 mL, larutan mempunyai bacaan absorban 0.388 pada 455nm. Dari keluk penentukuran, absorban ini sepadan dengan 3.1 ppm kepekatan Cu. Kirakan kepekatan Cu dalam bahagian per juta dalam sampel asal.
Diberikan: JAR: Cu = 63.54 g/mol

(25 marks/*markah*)

(ii) If the density of the river water sample above was 1.00 g/mL, calculate the percent of copper in the water.

Jika ketumpatan air sungai di atas adalah 1.00 g/mL, kirakan peratus kuprum dalam air sungai tersebut.

(25 marks/*markah*)

4. [a] 0.200 g s ample of pyrolusite is analyzed for manganese content as follows:

Add 50.0mL of a 0.100M solution of ferrous ammonium sulfate to reduce the MnO_2 to Mn^{2+}. After reduction is complete, the excess ferrous ion is titrated in acid solution with 0.0200M $KMnO_4$, requiring 15.0 mL. Calculate the percent manganese in the sample as MnO_2.

Given: The reaction between Fe^{2+} and MnO_4^- is:

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

The reaction between Fe^{2+} and MnO_2 is:

$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$

Given: Atomic weight of Mn = 54.94, O = 15.99 g/mol

0.200 g sampel pirolusit dianalisa untuk menentukan kandungan mangan seperti berikut:

Tambahkan satu isipadu 50.0mL 0.100M larutan ferrus ammonium sulfat untuk menurunkan MnO_2 to Mn^{2+}. Selepas penurunan lengkap, pentitratan ion ferrus yang berlebihan dalam larutan berasid memerlukan sebanyak 15 mL 0.0200M $KMnO_4$. Kirakan peratus mangan dalam sampel sebagai MnO_2.

Diberikan: Tindakbalas di antara Fe^{2+} dan MnO_4^- adalah:

$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Tindakbalas di antara Fe^{2+} dan MnO_2 adalah:

$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O$

Diberikan: Berat atom bagi Mn = 54.94, O = 15.99 g/mol

(50 marks/*markah)*

[b] (i) Calculate the pH of a buffer prepared by mixing 0.250 mol of acetic acid with 0.100 mol of sodium acetate and diluting to 1.00L. Given: K_a (CH_3COOH) = 1.75×10^{-5}

Kirakan pH selepas satu larutan tampan yang disediakan dengan percampuran 0.250 *mol asid asetik dengan 0.100 mol natrium asetat dan dicairkan kepada 1.00L.*
Diberikan: K_a (CH_3COOH) = 1.75×10^{-5}

(25 marks/*markah*)

(ii) Calculate the pH when 10.0 mL of this buffer is diluted to 250 mL with water.

Kirakan pH apabila 10.0 mL larutan tampan ini dicairkan kepada 250 mL dengan air.

(25 marks/*markah*)

5. [a] 300.0 mg sample containing phosphoric acid and inert material was diluted with water and 0.05 M NaOH according to the reaction below:

$H_3PO_4 + 2\ NaOH \rightarrow Na_2HPO_4 + 2\ H_2O$
(analyte) (titrant)

The end point was reached after 29.0 mL of titrant was added. Calculate the % H_3PO_4 in the sample.

Given: At. wt. of H = 1.0, P = 31.0 and O = 16.0 g/mol

300.0 mg sampel yang mengandungi asid fosforik dan bahan lengai dicairkan dengan air dan 0.05 M NaOH mengikut tindakbalas berikut:

$H_3PO_4 + 2\ NaOH \rightarrow Na_2HPO_4 + 2\ H_2O$
(analit) (titran)

Titik akhir dicapai selepas penambahan sebanyak 29.0 mL titran. Kirakan % H_3PO_4 dalam sampel.

Diberikan : JAR bagi H = 1.0*, P = 31.0 dan O = 16.0 g/mol*

(30 marks/*markah*)

[b] 750.0 mg sample of iron ore was dissolved in acid and treated to oxidize all of the iron to ferric iron. After destroying any remaining oxidizing agent, excess KI was added. The liberated I_2 required 28.50mL of 0.0750 M $Na_2S_2O_3$ for titration. What is the % of Fe in the sample?

Given the reaction equation:

$2\ Fe^{3+} + 2I^- \rightarrow 2\ Fe^{2+} + I_2$ (analyte)

$I_2 + 2S_20_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ (titrant)

Given: At. wt. of Fe = 55.85 g/mol

750.0 mg sampel bijih besi dilarutkan dalam asid dan dirawat untuk mengoksidakan kesemua besi kepada ion ferik. Selepas penyingkiran baki agen pengoksidaan, KI berlebihan ditambahkan. I_2 yang terbebas memerlukan sebanyak 28.50 mL isipadu 0.0750 M $Na_2S_2O_3$ bagi pentitratan. Berapakah % Fe dalam sampel?

Diberikan persamaan tindakbalas berikut:

$2\ Fe^{3+} + 2I^- \rightarrow 2\ Fe^{2+} + I_2$ *(analit)*

$I_2 + 2S_20_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$ *(titran)*

Diberikan: JAR bagi Fe = 55.85 g/mol

(30 marks/*markah*)

[c] A 0.1428 g sample of carbonate rock was pulverized and heated in a closed system causing the evolution of CO_2 according to the reaction below:

$$M_xCO_3 \rightarrow M_xO + CO_{2\ (g)}$$

A stream of nitrogen was used to sweep the CO_2 into 100.0 mL of 0.05172 M NaOH solution giving the reaction equation below:

$$CO_{2(g)} + 2\ NaOH \rightarrow Na_2CO_3 + H_2O$$

The excess NaOH required 28.14 mL of 0.1788 M HCl for titration. Calculate the amount of carbonate in the sample as % $CaCO_3$

Given: At. wt. of Ca = 40.0, C= 12.0 g/mole, O = 16.0 g/mole

0.1428 g sampel batuan karbonat dikisarkan halus dan dibakar dalam satu sistem tertutup dan membebaskan gas CO_2 mengikut tindakbalas berikut

$$M_xCO_3 \rightarrow M_xO + CO_{2\ (g)}$$

Gas nitrogen dialirkan untuk menolak keluar CO_2 masuk ke dalam satu larutan 100 mL 0.05172 M NaOH, memberikan persamaan tindakbalas berikut:

$$CO_{2(g)} + 2\ NaOH \rightarrow Na_2CO_3 + H_2O$$

NaOH yang berlebihan, yang tidak bertindakbalas, memerlukan sebanyak 28.14 mL isipadu 0.1788 M HCl bagi pentitratan. Kirakan amaun karbonat dalam sampel sebagai % $CaCO_3$.

Diberikan: JAR bagi Ca = 40.0, C= 12.0 g/mol, O = 16.0 g/mol

(40 marks/*markah*)

6. [a] Beer-Bouguer-Lambert's law, or more commonly known as Beer's law is important in the analysis of a mixture by spectrophotometry.

Hukum Beer-Bouguer-Lambert, atau lebih kenali sebagai Hukum Beer adalah penting dalam analisis satu campuran secara spektrofotometri.

(i) Derive mathematically Beer's law.
Terbitkan secara matematik Hukum Beer.

(ii) Show the relationship between absorptivity and molar absorptivity, Є.
What is the relationship between absorptivity and extinction coefficient?
Tunjukkan hubungan di antara absorptiviti dan absorptiviti molar, Є.
Apakah hubungan di antara absorptiviti dan koefisien "extinction"?

(iii) List ***FIVE*** conditions needed to ensure the validity of Beer's law.
Describe in brief ***TWO*** factors (with an example each) that may contribute to the deviation in Beer's law.
*Senaraikan **LIMA** keadaan yang diperlukan untuk memastikan kesahihan Hukum Beer.*
*Huraikan secara ringkas, **DUA** faktor (dengan contoh) yang mungkin menyebabkan sisihan kepada Hukum Beer.*

(50 marks/*markah*)

[b] A sample of unknown concentration, N, was put into a 2.0-cm cell. To determine the concentration, a spectrometer was employed. If transmission of light was 70% at a wavelength of 1.5 cm^{-1} g^{-1} L, calculate the concentration of N.

Satu sampel yang tak diketahui kepekatan, N, diletakkan dalam satu sel berukuran 2.0 cm. Satu spektrometer digunakan untuk menentukan kepekatannya. Jika cahaya yang terhantar adalah 70% pada jarak gelombang 1.5 cm^{-1} g^{-1} L, kirakan kepekatan N.

(20 marks/*markah*)

[c] A chemical substance consisting of X and Y, dissolving in water, exhibits strong absorbance at A nm ($\epsilon = 3.14 \times 10^4$). 0.2 g of this chemical substance is dissolved in water and diluted to 100 mL. A 1.0 mL aliquot was taken and diluted to 200 mL for measurement. If this final solution exhibits an absorbance of 0.385 at wavelength A in a 1.0-cm cell:

Satu bahan kimia yang mengandungi X dan Y, yang terlarut dalam air, mempamerkan absorban yang kuat pada A nm ($\epsilon = 3.14 \times 10^4$). Sebanyak 0.2 g bahan kimia ini dilarutkan dalam air dan dicairkan kepada 100 mL. Satu isipadu, alikuot 1.0 mL telah diambil dan dicairkan kepada 200 mL untuk pengukuran. Jika larutan akhir ini mempamerkan nilai absorban, 0.385 pada jarakgelombang A dalam satu sel 1.0-cm:

(i) Calculate the formula weight of substance XY.
Kirakan berat formula bahan XY.

(ii) Deduce the possible molecular formula if the atomic weights of X and Y are given as 25 and 150 respectively.
Hasilkan formula molekul yang mungkin jika berat atom X dan Y adalah masing-masing 25 dan 150.

(30 marks/*markah*)

7. [a] Define absorption, absorbance, transmittance and fluorescence.

Takrifkan penyerapan, absorbans, transmitan dan pendaflor.

(20 marks/*markah*)

[b] Briefly explain FOUR types of interferences that may affect emission and absorption. Include examples of each and how these interferences could be suppressed, minimized or avoided.

Terangkan secara ringkas, EMPAT jenis gangguan yang mungkin mempengaruhi pemancaran dan penyerapan. Berikan contoh bagi setiap satu dan tunjukkan bagaimana gangguan ini boleh dihalang, diminimakan atau dielakkan.

(40 marks/*markah*)

[c] Using a table and the aid of a sketch, show the comparisons between the operation of a single-beam and a dual-beam spectrophotometer.

Menggunakan satu jadual dan bantuan lakaran, tunjukkan perbandingan di antara operasi satu spektrofotometer bim tunggal dan bim dual.

(20 marks/*markah*)

[d] Briefly describe the principles of atomic absorption spectrophotometry. Subsequently, list the advantages and disadvantages.

Terangkan secara ringkas prinsip-prinsip spektrofotometri serapan atom. Seterusnya, senaraikan kebaikan dan keburukannya.

(20 marks/*markah*)

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APPENDIX / *LAMPIRAN*

Table A: Values of t for ν ,Degrees of freedom for various confidence level

Jadual A: Nilai-nilai t bagi darjah kebebasan, ν pada pelbagai paras keyakinan

	Confidence Level *(Paras Keyakinan)*			
ν	**90 %**	**95 %**	**99 %**	**99.5 %**
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

* ν = N -1 = degrees of freedom

Table B: Rejection quotient, Q, at different confidence limits

Jadual B: Rejection quotient, Q, pada had keyakinan berbeza

No. of Observations	Confidence Level *(Paras Keyakinan)*		
	Q_{90}	Q_{95}	Q_{99}
3	**0.941**	**0.970**	**0.994**
4	**0.765**	**0.829**	**0.926**
5	**0.642**	**0.710**	**0.821**
6	**0.560**	**0.625**	**0.740**
7	**0.507**	**0.568**	**0.680**
8	**0.468**	**0.526**	**0.634**
9	**0.437**	**0.493**	**0.598**
10	**0.412**	**0.466**	**0.568**
15	**0.338**	**0.384**	**0.475**
20	**0.300**	**0.342**	**0.425**
25	**0.277**	**0.317**	**0.393**
30	**0.260**	**0.298**	**0.372**

*Adapted from D.B. Rorabacher. Anal. Chem., 63 (1991) 139.